Bull. Environ. Contam. Toxicol. (2004) 72:954–961
© 2004 Springer-Verlag New York, LLC
DOI: 10.1007/s00128-004-0336-x

Bulletin of Environmental Contamination and Toxicology

Accumulation Features of Organochlorine Pesticides Residues in Soils around Beijing Guanting Reservoir

Z. Hong, L. Yonglong, W. Tieyu, S. Yajuan

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Post Office Box 2871, Beijing 10085, People's Republic of China

Received: 17 July 2003/Accepted: 22 January 2004

Persistent organic pollutants (POPs) have been the major environmental issue, drawing much scientific and public attention due to their high bioaccumulation potential, persistence and high toxicities to non-target organisms (Jones and Voogt, 1999; Loganathan and Kannan, 1994). In China, most of the pesticides produced and used from the 1960s to 1980s are organochlorine pesticides (OCPs) that of POPs kind. During the past years, over 600,000 t of OCPs have been produced in China and the uncontrolled use of OCPs in agriculture contributed to high concentrations of their residues detected in the environment (Hua et al. 1992). The awareness of POPs has been increasing these years, as a considerable number of past studies have reported their residuals in the coastal sediments, surface waters, food and vegetables, wild animals and human breast milks (Wang et al. 2003; Ma et al, 2001). However, more attention was paid to aquatic ecosystems while less to terrestrial ecosystems in China.

Guanting reservoir, located in the northwest of Beijing, is one of the five major water systems of Beijing. It used to be a drinking water source of Beijing before 1997, but the water quality of reservoir has been degraded from grade Ⅱ to grade Ⅳ in terms of the national standards for the following reasons: 1) A variety of small industrial complexes are located in its upper reach and poured a large amount of polluted water into the river; 2) a large quantity of domestic sewage is dumped into the water areas; 3) the upper water quantity has been decreasing because of drought and farm irrigation; and 4) non-point farming pollution is a big source of Guanting Reservoir contamination.

This paper is intended to study the current status and accumulation features of soil pollution by OCPs at Guanting Reservoir area, to distinguish the major sources of soil pollution by using statistic methods, and to find out whether the concentrations of OCPs are different between farm soils and orchard soils, and whether sampling locations make a significant difference in the concentrations of OCPs.

MATERIALS AND METHODS

A composite stock standard solution of OCPs including α-, β-,γ- and δ-HCH and

---

Correspondence to: L. Yonglong

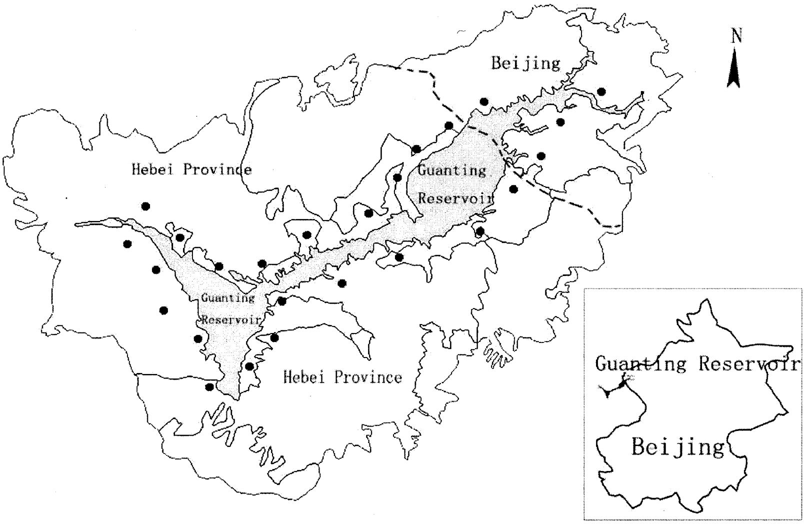

Figure 1. Geographical location of sampling sites.

p,p'-DDT, o,p'-DDT, p,p'-DDE, p,p'-DDD was obtained from National Research Center for Certified Reference Materials of China at a concentration of 100 mg/L and then diluted to a desired concentration. All solvents used were of analytical grade and redistilled to remove impurities prior to use.

Soil samples were collected around the Guanting Reservoir at the late fall in 2002. The detailed sampling locations are shown in Figure 1. Each sample was a composite of soil subsamples taken from the top 20 cm of five sites and was mixed, sieved (1mm) and freeze-dried prior to analysis. Site descriptions were registered at the time of sampling to record the sample locations (e.g. SE means Southeast of Guanting Reservoir), land use types (farm or orchard) and major environmental features.

All soil samples were extracted and cleaned up following the standard operating procedures as specified in the State Environmental Protection Administration of China method (SEPA, 1993). Approximately 10-g of freeze dried sample were transferred to 250-ml Erlenmeyer flask, activated copper powder was added to remove sulfate, followed by adding 80 ml hexane- dichloromethane mixture (1:1 v/v). Extracted with sonication for 60min, then stand overnight and sonicated 40 min again. The extract was decanted, another 20-ml hexane was added and sonicated for 20 min, the two extracts were combined and concentrated on a 10 ml rotary evaporator keeping the temperature of water bath below 30℃. The extract was removed to a separating funnel and added 10ml concentrated sulfuric acid to get rid of the impurities 2-3 times. The organic phase was washed with 50ml 5% sodium chloride solution twice. The extract was concentrated to about 1ml using a rotary evaporator as above, and further purified with 2-g silica gel and 2-g Florisil column (I.D. 12mm). Before the extract was loaded, 2g of anhydrous sodium sulfate was added at the top. The elution was done with 20-ml n-hexane, then 20-ml n-hexane containing 10% dichloromethane. With a gentle stream of clean dry nitrogen, the solution was evaporated down to 0.5 ml for GC analysis.

The GC system was operated in a splitless mode and 1μL of the extract was injected into the GC system for separating the OCPs. The oven temperature was raised from 80℃ to 200℃ at a rate of 10℃/min, hold for 1 min, and then programmed to 270℃ at 5℃/min, hold for 5 min. The injector and detector were maintained at 250℃ and 280℃, respectively. High purity nitrogen was used as carrier gas at a rate of 1.0ml/min and make-up gas was 49ml/min. GC peaks were identified with the accurate assignment of retention times of each standard (±1%).

The residues of OCPs were quantitatively determined by comparing the area under each peak with the area under the standard peak. For every set of 8 samples, a procedural blank and a spiked sample consisting of all chemicals were run to check the interference and cross-contamination. The correlation coefficients of calibration curves of OCPs were all greater than 0.998. The limits of detection (LDs) of OCPs were described as 3 of signal-to-noise ratio (S/N). The detection limits of α-, β-, γ- and δ-HCH were 0.046, 0.154, 0.055, 0.063 ng g^{-1}, and those of p,p'-DDT, o,p'-DDT, p,p'-DDE, p,p'-DDD were 0.058, 0.066, 0.270, and 1.234 ng g^{-1}. The recoveries of α-, β-, γ- and δ-HCH with spiked samples were 96, 83, 92, 80% and those of p,p'-DDT, o,p'-DDT, p,p'-DDE, p,p'-DDD were 103, 89, 85, 82%. The Relative Standard Deviation varied from 5 to 12.

Nonparametric method was used to test if there was a significant difference of OCPs in different groups (data were grouped by land use type or by sampling location). Nonparametric test is an alternative to rectify the acquired data that do not meet assumptions of ANOVA analysis and it does not require a normal distribution.

RESULTS AND DISCUSSION

Table 1 and Table 2 showed the results of the concentrations of HCH isomers and DDT isomers in 25 soil samples collected from Guanting reservoir, in which ∑HCH and ∑DDT represented their total concentration respectively, ratio1 represented α-HCH to γ-HCH, and ratio2 represented DDE plus DDD to DDT. HCH was detected with levels ranging from Nd to 19.23 ng g^{-1} of dry weight and DDT was detected with levels ranging from Nd to 176.01 ng g^{-1} of dry weight. DDT was more abundant than HCH.

Commercial HCH mixture contains 55–80% α-HCH, 5-14% β-HCH, 12-15% γ-HCH, 2-10% δ-HCH and other chlororganic compounds, respectively (Kim et al, 2002). In soils, average half-lives of 20–50 days for δ-HCH and 20 weeks for α-HCH were observed (FAO, 2000). The ratio of α-HCH/γ-HCH, 4-7 in technical mixture HCH, can be an indicator reflects the degradation or use of a mixture of HCHs (Kim et al, 2002). As shown in Table 1 and Table 2, the concentration of

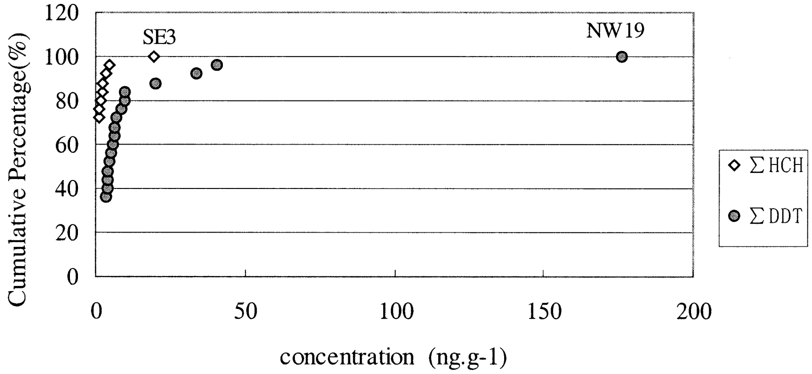

Figure 2. Cumulative percentage over Concentrations of ∑HCH and ∑DDT.

β-HCH in Guanting Reservoir soils was much higher than that of other HCH isomers. The ratio of α- to γ-HCH (ratiol) was 0-3.36 (with 1.73 as median), lower than those in the mixture HCH. The results indicated that long time has elapsed since the use of HCH in the area.

Technical DDT product generally contains 75% p,p'-DDT, 15% o,p'-DDT, 5% p,p'-DDE, <0.5% p,p'-DDD, <0.5% o,p'-DDD, < 0.5% o,p'-DDE and <0.5% unidentified compounds (WHO, 1979). DDT isomers have a long persistence in environment and gradually degrade to DDE and DDD under the aerobic and anaerobic condition. The percentage of DDE and DDD has been regarded as an indication of no or decreasing new input to environment (Aguilar, 1982). The DDT isomers have the concentrations in the order of p,p'-DDE> p,p'-DDT > o,p'-DDT>p,p'-DDD. The ratio of DDE plus DDD to DDT (ratio2) was 0.24 to 4.06 (with 0.86 as median). The predominance of DDE isomer indicates that extensive contamination of DDT occurred in the past. However, high concentration of p,p'-DDT indicates a new input of DDT compounds.

The cumulative distribution of concentrations of ∑HCH and ∑DDT was shown in Figure 2. It was noticed that a vast majority of the points were compressed at the upper left of the graph between 0 and 50ng g-1. As for ∑HCH, in more than 50% of the sites HCH was not detected, in 96% sites the concentration of HCH ranged from 0.00 to 3.31 ng g^{-1}. There was a single point, SE3, valued 19.23 ng g^{-1}, nearly 5 times larger than any other points in the graph. As regards ∑DDT, in 16% of the sites DDT was not detected, in 96% sites the concentrations of DDT was lower than 50 ng g^{-1}, while NW19, with a magnitude value of 176.01 ng g^{-1}, greater than any other points.

With outlier data points (SE3 and NW19) removed, a skew distribution of ∑HCH and ∑DDT were found. Then nonparametric method (Kruskal-Wallis Test for K Independent Samples) was used to test if there was a significant difference of ∑HCH and ∑DDT in different land use types or sampling locations. The results

Table 1. HCH isomers and DDT isomers in the soil of Guanting Reservoir (ng g^{-1})

Site No.	Sampling Location	Land use type	α-HCH	β-HCH	γ-HCH	δ-HCH	p,p'-DDE	p,p'-DDD	o,p'-DDT	p,p'-DDT	∑HCH	∑DDT	Ratio1	Ratio 2
SE1	Southeast	Orchard	0.20	0.80	Nd	Nd	2.13	Nd	Nd	4.98	1.01	7.11	-	0.43
SE2		Farm	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	-	-
SE3		Orchard	0.22	19.01	Nd	Nd	7.49	0.19	0.42	1.47	19.23	9.57	-	4.06
SE4		Farm	Nd	Nd	Nd	Nd	3.08	0.18	0.84	1.90	Nd	6.01	-	1.19
SE5		Farm	Nd	Nd	Nd	Nd	0.16	Nd	Nd	0.68	Nd	0.84	-	0.24
SW6	Southwest	Farm	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	-	-
SW7		Orchard	0.27	1.40	0.16	0.29	2.29	0.20	Nd	0.96	2.11	3.45	1.66	2.60
SW8		Farm	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	-	0
SW9		Farm	0.07	1.04	Nd	Nd	1.60	0.12	0.72	1.27	1.11	3.71	-	0.86
SW10		Orchard	Nd	Nd	Nd	Nd	2.02	0.30	0.45	2.72	Nd	5.49	-	0.73
W11	West	Farm	Nd	1.78	0.19	0.40	1.14	Nd	Nd	3.80	2.37	4.94	0.00	0.30
W12		Orchard	0.21	0.37	Nd	Nd	6.61	0.18	Nd	1.74	0.58	8.53	-	3.90
W13		Orchard	0.18	0.33	Nd	Nd	2.58	Nd	Nd	0.86	0.51	3.44	-	3.00
W14		Farm	Nd	Nd	Nd	Nd	0.51	0.17	Nd	0.93	Nd	1.61	-	0.73
W15		Farm	Nd	Nd	Nd	Nd	2.48	Nd	Nd	1.94	Nd	4.42	-	1.28
NW16	Northwest	Farm	Nd	Nd	Nd	Nd	2.03	0.38	0.51	1.33	Nd	4.25	-	1.31
NW17		Farm	Nd	Nd	Nd	Nd	0.63	Nd	Nd	Nd	Nd	0.63	-	0
NW18		Orchard	0.37	2.39	0.20	0.36	8.35	Nd	6.01	5.87	3.31	20.22	1.79	0.70
NW19		Orchard	0.78	2.04	0.43	1.32	77.84	3.37	11.71	83.08	4.57	176.01	1.81	0.86
NW20		Farm	0.26	0.68	0.23	0.78	3.89	0.19	0.28	2.19	1.95	6.55	1.10	1.65
NE21	Northeast	Farm	0.23	0.71	Nd	Nd	8.22	1.43	2.19	28.64	0.94	40.47	-	0.31

Table 1. Continued

NE22	Orchard	Nd	Nd	Nd	Nd	13.96	1.20	1.16	17.29	Nd	33.61	-	0.82
NE23	Farm	0.26	0.76	0.08	Nd	1.55	0.30	0.35	1.74	1.10	3.94	3.36	0.88
NE24	Orchard	0.12	0.63	Nd	Nd	3.13	Nd	Nd	6.48	0.76	9.61	-	0.48
NE25	Farm	Nd	Nd	Nd	Nd	1.65	0.19	Nd	Nd	Nd	1.84	-	0

Nd= not detected

All concentrations were given in units of ng g^{-1} of dry weight.

Ratio 1= α-HCH/γ-HCH, Ratio 2= (DDD+DDE)/DDT

Table 2. Descriptive Statistics of HCH isomers and DDT isomers in Guanting reservoir area

	α-HCH	β-HCH	γ-HCH	δ-HCH	p,p'-DDE	p,p'-DDD	o,p'-DDT	p,p'-DDT	∑HCH	∑DDT	Ratio1	Ratio 2
Median	0.00	0.32	0.00	0.13	2.13	0.17	0.00	1.74	0.50	4.42	1.73	0.86
Minimum	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.24
Maximum	0.78	19.01	0.43	1.32	77.84	3.37	11.71	83.08	19.23	176.01	3.36	4.06
Frequency of Nd (%)	52	48	76	80	12	44	56	20	48	12		
SD	0.18	3.77	0.11	0.31	15.31	0.72	2.56	17.09	3.86	35.12		
Skewness[1]	2.11	4.72	2.32	2.96	4.63	3.50	3.64	4.09	4.30	4.42		
Kurtosis	6.10	23.04	5.49	9.18	22.36	13.43	13.92	17.95	19.90	20.68		

All concentrations were given in units of ng g^{-1} of dry weight.

SD= Standard deviation

[1] Skewness shows a positive skew distribution

Ratio 1= α-HCH/γ-HCH, Ratio 2= (DDD+DDE)/DDT

Table 3. Nonparametric test for the sample distribution.

Grouping variable	Statistics	∑HCH	∑DDT
Land use type	Chi-Square	4.24	7.70
	df	1	1
	Sig.	0.04*	0.006*
Sampling location	Chi-Square	1.18	5.31
	df	4	4
	Sig.	0.88	0.26

*: Significance level, *P*<0.05

Table 4. Comparison of OCPs levels (ng/g) from other areas in China.

Area	Survey year	Source	HCH	DDT	Reference
Shenyang city	1987	Soil	970	530	Niu et al, 1991
Ahhui province	1989	Soil	150	361	Yue et al, 1990
Inner mongolia	1995	Soil	28.9	----	Wu et al, 1995
Ninbo city	1999	Soil	6.0	265.4	Zhao et al,2001
Jiaxing city	2001	Soil	34.7	39.5	Zhao et al, 2003
Guanting reservoir	2002	Soil	0.50	4.42	Present study
Guanting reservoir	2000	Sediment	0.67	15.15	Ma et al, 2001
Guanting reservoir	2000	Water	9.1*	3.1*	Wang et al, 2003

*: in ng/L

showed in Table 3 that a statistical significance was accepted in sampling distribution when data grouped by land use types (Sig.<0.05), but no significance when data grouped by sampling locations (Sig.>0.05). This showed that the concentrations of OCPs in farm soils were lower than those in orchard soils. It could be concluded that the major sources of OCPs were from orchard soils; while there were no significant difference in OCPs concentrations in different orientation soils of Guangting Reservoir area.

Compared the levels of OCPs in soil in Guanting area with that in other areas of China (Table 4), the average concentration was lower than that in other areas. The residue levels of OCPs in the earlier period were much higher than those in recent years, which indicated that concentrations of OCPs have decreased significantly since the use of those compounds ceased in China. In Guanting reservoir, the levels of OCPs in soil were slightly lower than those in sediment and in water. It indicated that concentrations of DDT and HCH in Guanting Reservoir were recently declining slowly, reflecting a complex interrelationship among sediment, surface water, soil and air.

This investigation revealed the soil contamination by OCPs in the Guanting Reservoir areas. A heavier contamination was found in the orchard soil than in the farm soil. Despite the low concentrations of OCPs in the soil, some substitute of DDT may still be used in the study area. Although the contamination levels detected here weren't high enough to cause acute effects, they could have negative impacts on the local terrestrial and aquatic ecosystems in a long term.

Acknowledgments. We thank Professor Jiang Guibing and Dr. Yang Ruiqiang for technical assistance. This work was supported by the Knowledge Innovation Program of the Chinese Academy of Sciences, with Grant No. KZCX2-414.

REFERENCES

Aguilar, A. (1982) Relationship of DDE/ΣDDT in marine mammals to the chronology of DDT input into the ecosystem. Canadian J Fish Aquat Sci 41:840-844

FAO Information Division (2000) FAO PESTICIDE DISPOSAL SERIES 8: Assessing soil contamination (A reference manual), Rome

G.B. Loganathan, K. Kannan (1994) Global organochlorine contamination trends: an overview. Ambio 23: 187-190

Hua Xiaomei, Shan Zhengjun (1996) The production and application of pesticides and factor analysis of their pollution in environment in China. Adv Environ Sci 44:33-45 (in Chinese)

K.C.Jones, P.de Voogt (1999) Persistent organic pollutants(POPs): state of the science. Environ Pollut 100: 209-221

Kim J.H., Smith A. (2001) Distribution of organochlorine pesticides in soil from South Korea. Chemosphere 43: 137-140

Kim S.-K., Oh J.R., Shim W.J., Lee D.H., Yim U.H., Hong S.H., Shin Y.B., Lee D.S. (2002) Geographical distribution and accumulation features of organochlorine residues in bivalves from coastal areas of South Korea. Mar Pollut Bull 45:268-279

Ma Mei, Wang Zijian, Anders Sodergren (2001) Contamination of PCBs and organochlorinated pesticides in the sediment samples of Guanting Reservoir and Yongding River. Environ Chem 20: 238-243 (in Chinese)

Niu Sen, Zhou Yanming, Jiang Yuwen, He Zhenchang (1991) Report on determining residues of organochlorine pesticides in vegetables and soils in Shenyang city. J Shenyang Agri Univ 22:140-144 (in Chinese)

State Environmental Protection Administration of China (1993) Soil quality --Determination of BHC and DDT--Gas chromatography. SEPA, Beijing

World Health Organization (1979) DDT and its derivatives. WHO, New York.

Wu Liji, Fu Yinsheng, Zhang Fuguo (1995) The determined and studied the organic chlorid pesticides residues in the fine herbage and soil of Hulunbule grass land. Environ Eng 13:53-55 (in Chinese)

X.T. Wang, S.G. Chu, X.B. Xu (2003) Organochlorine pesticide residues in water from Guanting Reservoir and Yongding River, China. Bull Environ Contam Toxicol 70:351-358

Yue Yongde, Hua Rimao, Zhu Lizhen, Zhu suwen, Chen Dingding (1990) Residual form and level of BHC and DDT in agroenvironment of Anhui. J Anhui Agri Coll 17:194-197 (in Chinese)

Zhao Lin, Ma Yongjun (2001) Organochlorine pesticide residues in agricultural environment. Agri Environ Develop 1: 37-39 (in Chinese)

Zhao Yuwan, Chen Kun, Ma Xinyuan, Yao Kaiyan (2002) A study on the residue of the organochloride pesticide in soil and rice. Zhejiang Prev Med 14:1-3